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No.

IN THE

Supreme Court of the United States

OCTOBER TERM, 1985

BLOCK DRUG COMPANY, INC., et al.,

Petitioners,

vs.

MILTON HODOSH and RICHARDSON-VICKS, INC.,

Respondents.

PETITION FOR A WRIT OF CERTIORARI TO
THE UNITED STATES COURT OF APPEALS FOR THE FEDERAL CIRCUIT

APPENDIX

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United States Patent [19]

Hodosh

[11] **3,863,006**

[45] **Jan. 28, 1975**

[54] **METHOD FOR DESENSITIZING TEETH**

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[21] Appl. No.: **327,758**

[52] U.S. Cl. 424/49

[51] Int. Cl. A61k 7/16

[58] Field of Search 424/49-58

[56] **References Cited**

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Primary Examiner—Richard L. Huff

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[57] **ABSTRACT**

A compound and method for desensitizing hypersensitive teeth, and specifically hypersensitive dentin and cementum, the essential ingredient of said compound comprising a nitrate of potassium, lithium or sodium, and the method comprising the application of said compound in aqueous solution or nontoxic paste form to the sensitive area.

6 Claims, No Drawings

METHOD FOR DESENSITIZING TEETH

BACKGROUND AND SUMMARY OF THE INVENTION

The present invention relates to a compound and treatment for eliminating or, at the very least, greatly reducing, discomfort and pain caused by tooth hypersensitivity or exposed cementum and/or dentin.

It is becoming increasingly apparent that the problem of tooth hypersensitivity affects a far greater number of people than previously suspected. People suffering from this annoying condition may react painfully to heated or chilled foods, citric acid or sweets, or other every-day stimuli, including toothbrush contact. The problem is especially prevalent in adults who have lost some of the normal protective enamel sheathing on tooth surfaces because of erosion, abrasion, caries, chipping of the enamel, or in whom recession of the gingiva has exposed tooth dentin and/or cementum. However, tooth hypersensitivity is now being found to exist even in the absence of any of the foregoing.

Attempts have heretofore been made to eliminate or at least reduce the painful effects of tooth hypersensitivity or of exposed cementum and/or dentin; but, for various reasons, many of these previous attempts have not been completely successful. For example, silver nitrate is a known desensitizer, but it is such a powerful oxidant that it may burn or otherwise irritate the gum tissues, as well as causing discoloration of the teeth. In another approach, a finely ground paste of dicalcium acid phosphate was rubbed into the exposed, sensitive tooth roots of various patients suffering from hypersensitivity with some success, based on the observation that the paste crystallized and blocked the dentinal tubules, thereby apparently protecting the sensitive, nerve-filled pulp inside. Still another approach involves the use of strontium ions, as disclosed in U.S. Pat. No. 3,122,483 dated Feb. 25, 1964.

In spite of the above, the search goes on for a desensitizer which may be easily and economically produced, which may be easily applied to hypersensitive tooth areas, which is effective in achieving the desired desensitizing function without irritation of the gums and discoloration of the teeth, and which has a longer lasting effect. It is to the accomplishment of these objectives that the present invention is directed.

DESCRIPTION OF THE INVENTION

It has been found that the nitrate of any one of the following alkali metals has amazing and unusual desensitizing action when applied to hypersensitive teeth or exposed dentin and/or cementum. Specifically, potassium nitrate, lithium nitrate, and sodium nitrate have been found to be extremely effective in this regard, and potassium nitrate, in particular, has been found to be both extremely effective and relatively long lasting in its effect. However, lithium nitrate and sodium nitrate are also effective, and none of these nitrates are irritating to the gingiva, nor do they discolor the teeth. Other potassium salts have been tried, but none appear to be as effective as potassium nitrate insofar as desensitizing is concerned. Also, other metal nitrates do not seem to be as effective and satisfactory. Thus, for reasons not completely known, potassium nitrate achieves an unusually effective desensitizing result, and to a somewhat lesser extent, so do the other alkali metal nitrates, namely, lithium nitrate and sodium nitrate.

The other alkali metals, namely, rubidium, cesium, and francium, are extremely rare and expensive and hence are not feasible nor practicable for use in the present invention. In addition, francium is radioactive.

In utilizing potassium nitrate as a desensitizing agent, it is simply necessary to dissolve potassium nitrate crystals in a liquid solution, preferably water; and then the solution so formed is liberally applied to the hypersensitive area by means of cotton or the like. It has specifically been found that an aqueous solution comprising 5 percent by weight of potassium nitrate works extremely well. On the other hand, an aqueous solution comprising 1 percent by weight of potassium nitrate is also effective, but not to the extent that a more concentrated solution is. An aqueous solution of potassium nitrate saturates when the solution contains approximately 20 percent by weight potassium nitrate, and such a saturated solution may also be used, but the results of a saturated solution are not sufficiently beneficial over that of a 5 percent solution to justify the inclusion of the additional potassium nitrate.

As previously stated, the liberal application of an aqueous solution of potassium nitrate to the hypersensitive area results in almost immediate and extremely pronounced desensitization of the hypersensitive area, without any irritation of the gingiva, nor any discoloration of the teeth. In addition, the desensitization effect remains for a relatively long time, and in some cases for days.

In addition to applying the nitrate of potassium, lithium or sodium to the hypersensitive area in the form of an aqueous solution, it is also possible to incorporate the nitrate in a nontoxic paste which would then be applied to the sensitive area. For example, a paste was formulated as follows:

	Percent
Potassium nitrate	10.0
Water	34.2
Glycerin	25.0
Hydroxyethylcellulose	1.6
Polyoxyethylene sorbitan monolaurate	2.0
Micronized silica	24.0
Spearmint oil	1.0
Saccharin	0.2

(All percentages by weight)

The above paste, which actually has ingredients to function as a toothpaste in addition to performing a desensitizing function, when applied to a hypersensitive area in a patient's mouth, achieves basically the same desensitizing results as where the application is by means of an aqueous solution. More specifically, relatively extreme desensitizing took place without any irritation of the gingivae or discoloration of the teeth. When used in a paste of this type, the compound obviously has a preventive function, as well as a treatment function.

Although it is not positively known whether the desensitizing effect of the potassium nitrate is due to the oxidizing nature of the compound, or whether a crystallization takes place which blocks the dentinal tubules and hence protects the sensitive, nerve-filled pulp located therein, the fact remains that the use of potassium nitrate, and also lithium and sodium nitrate, whether in aqueous or paste form, results in desensitization of the hypersensitive area to an unexpected and

surprising degree without adversely affecting said area in any way, and said desensitizing effect has been found to be relatively long lasting.

As this invention may be embodied in several forms without departing from the spirit or essential characteristics thereof, the present embodiment is therefore illustrative and not restrictive, since the scope of the invention is defined by the appended claims rather than by the description preceding them, and all changes that fall within the metes and bounds of the claims or that form their functional as well as conjointly cooperative equivalents, are therefore intended to be embraced by these claims.

What is claimed is:

1. The method of desensitizing hypersensitive dentin and cementum by applying thereto an agent, the essential ingredient of which is a nitrate of one of the following alkali metals: potassium, lithium or sodium said nitrate comprising between 1 percent and 20 percent by weight of said agent.

2. The method of claim 1 further characterized in that said nitrate is potassium nitrate in an aqueous solution.

3. The method of claim 2 further characterized in that said potassium nitrate comprises approximately 5 percent (5%) by weight and saturation of said aqueous solution.

4. The method of claim 1 further characterized in that said nitrate is potassium nitrate mixed with a nontoxic paste.

5. The method of claim 4 further characterized in that said potassium nitrate comprises approximately ten percent (10%) by weight of said paste.

6. The method of desensitizing hypersensitive dentin and cementum by applying thereto an aqueous solution, the essential ingredient of which is potassium nitrate, said potassium nitrate comprising between 1% by weight and saturation of said aqueous solution.

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United States Patent Office 3,122,483 Patented Feb. 25, 1964

3,122,483

STRONTIUM ION TOOTHPASTE

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No Drawing. Filed July 22, 1960, Ser. No. 44,246
11 Claims. (Cl. 167—93)

The present invention relates generally to an improved dentrifice, and in particular it relates to an improved paste dentrifice effective in the treatment of hypersensitive dentin.

The condition known as hypersensitive dentin is quite prevalent. It may exhibit itself in response to various external stimuli on the surface of the teeth such as thermal changes, tactile stimuli, high osmotic pressures in the oral cavity, changes in pH, and other common circumstances virtually impossible to avoid. The problem is especially acute in adults who have lost some of the normal protective enamel sheathing on tooth surfaces because of erosion, abrasion, caries, chipping of the enamel, or in whom recession of the gingiva has exposed tooth dentin and cementum. However, certain stimuli such as cold, heat, and high sugar concentrations may evoke a painful response in children's teeth even when the teeth are in sound condition and the protective enamel tooth covering is still intact. The causes of painful hypersensitive dentin have never been completely explained since it has been demonstrated that calcified tooth structure itself does not contain nerve fiber. However, a generally accepted theory is that the dentinal tubules and odontoblastic fibrils in dentin, the normal functions of which are to produce calcified compounds in the tooth structure, are capable of transmitting neural impulses from the tooth structure to the dental pulp, which contains extremely sensitive nerve cells. The dentinal tubules and odontoblastic fibrils account in large part for the organic fraction of tooth dentin. It is known that both immature enamel and immature and mature dentin are higher in organic content than mature enamel, and thus probably have a higher content of dentinal tubules and odontoblastic fibrils than tooth enamel for the transmission of the above mentioned neural impulses. This circumstance would explain the greater sensitivity of immature teeth and exposed dentin in mature teeth.

Many methods have been proposed for the treatment of hypersensitive dentin. Some of these include sodium fluoride solution, sodium silicofluoride solution, zinc chloride solution, formaldehyde solution, concentrated glycerin, silver nitrate solution, and other agents. However, all these proposed therapies suffer from one disadvantage or another. Some are potentially toxic to the user if accidentally ingested in large doses; others are tissue denaturants or coagulants to be used with great caution and only under professional supervision, and others may discolor the teeth. None are believed to be suitable for incorporation into a toothpaste for home use which would be effective, stable, and safe for continued periods of time.

It is, therefore, a principal object of the present invention to provide an improved dentifrice.

Another object of the present invention is to provide an improved paste dentifrice effective in the treatment of hyper-sensitive dentin.

Still another object of the present invention is to provide paste dentifrice compositions which will carry solutions of strontium compounds capable of releasing strontium ions to the calcified structures of the human teeth.

A further object of the present invention is to provide a means for individuals to bring into contact with their

teeth toothpaste containing solutions of water-soluble strontium compounds.

Still a further object of the present invention is to provide novel compositions of matter in the form of toothpastes which will allow the calcified tissues of the human mouth to adsorb strontium ions from solutions of water-soluble strontium compounds contained in the toothpaste.

An additional object of the invention is to provide a convenient, rapid, non-toxic, therapeutic method for the daily treatment and control of painful dentin, commonly known as hyper-sensitive dentin, by use of a toothpaste which releases strontium ions from solutions of water-soluble strontium compounds contained in the toothpaste during normal toothbrushing procedures.

Other objects and advantages of the invention will be apparent to those skilled in the art.

It has been discovered that solutions of water-soluble strontium compounds are particularly suitable for the therapy of hyper-sensitive dentin and are non-injurious to the tissues of the mouth. When applied to tooth surfaces, it is believed that an adsorption of strontium ions occurs on the odontoblastic fibrils or in the dentinal tubules thus blocking the transmission of neural impulses from the dentinal surface to the dental pulp. Since strontium ion is a normal constituent of tooth structure and since it has extremely low local and systemic toxicity, it is believed that this observation provides a useful therapeutic means for the dentist to control hypersensitive dentin by the application of simple water-soluble strontium compound solutions to the teeth of his patients.

The use of a surface active wetting agent with the water soluble strontium compound contained in the toothpaste has been found to be highly desirable, particularly when such wetting agent is a foaming type of detergent. In addition to serving the purpose of cleaning the teeth, the detergent enhances the effectiveness of the strontium ion as a desensitizing agent by facilitating penetration of strontium ions into tooth structure. The water-soluble strontium compound is advantageously incorporated along with the wetting agent in a toothpaste which includes enough water to dissolve a substantial percentage, or all, of the water-soluble strontium compound, a polishing agent and certain other ingredients including bodying and gelling agents, and other additives.

The incorporation of water-soluble strontium compounds in common water-containing toothpaste formulations so that treatment for hypersensitive dentin can be continued away from the dental office, however, has heretofore proven to be wholly unsuccessful because of the highly reactive chemical nature of the strontium ion. Most commercial dentifrices are formulated with inorganic chemical polishing agents of low solubility in which the cation is an alkaline earth metal such as calcium or magnesium. Calcium phosphates, calcium carbonate, calcium sulfate, magnesium hydroxide, magnesium phosphates, and magnesium carbonate are examples of commonly used polishing compounds. It is not feasible to incorporate water-soluble strontium compounds into water-containing toothpaste formulations of this nature because of the chemical reaction which will occur between the strontium ions from the water-soluble strontium compound and the anions of the alkaline earth metal polishing agent in the presence of water contained in the toothpaste with eventual partial to complete precipitation and removal from therapeutic utility of the originally soluble strontium compound.

Furthermore, the foaming agents used in normal tooth paste formulations are surface active wetting agents which are usually anionic in nature, consisting of long-chain fatty

fatty acid soaps, and fatty acids or alcohols etherified, esterified, or condensed with sulfates, phosphates, amino acids, polyalkylene oxides, or conjugated cyclic derivatives. Strontium ions will react with many of these surfactants in the presence of water contained in a toothpaste to produce insoluble strontium derivatives which can not then provide the cleansing and foaming action desirable in toothpastes after storage for prolonged periods.

In addition, many of the bodying and gelling agents employed in conventional toothpaste formulations are alkali-metal salts of high molecular weight carbohydrate or cellulosic polymers containing terminal carboxylic or sulfonic acid groups. These agents are not suitable for use with water-soluble strontium compounds held in solution because of the eventual reaction between the acid radicals with the strontium ion in the presence of water contained in the toothpaste, resulting in a loss of bodying properties in the finished toothpaste.

It has been found to be essential, therefore, to incorporate the water-soluble strontium compounds into water-containing toothpastes in which all major components are compatible with the strontium compounds; that is, that such toothpaste components will neither render inactive nor precipitate the strontium ion and the word compatible will herein be used in such sense both in the specification and in the appended claims. Examples of compatible polishing agents which have been employed for the purpose include strontium phosphates, strontium carbonate, micronized silica, and aluminum hydroxide. Examples of surface-active foaming agents which have been employed, demonstrating a high degree of compatibility with water-soluble strontium compounds, include the polyoxyethylene partial esters of polyhydric fatty acid derivatives, polyoxyethylene polyoxypropylene condensates, polyoxyethylene-fatty alcohol ethers, fatty acid N-methyl taurine condensates, and the like. Examples of compatible bodying agents which have been used include methylcelluloses, hydroxyethylcelluloses, and very high molecular weight polyoxyethylene polymers.

Other constituents incorporated in the water-containing toothpastes must also be compatible with water-soluble strontium compounds. For that reason, sodium benzoate is not used as a preservative since it will react with strontium ions in the presence of water contained in the toothpaste to produce an insoluble precipitate. Ascorbic acid, sodium bicarbonate, sodium N-lauroyl sarcosinate, sodium oxalate, sodium lauryl sulfate, sodium fluoride, stannous fluoride, diammonium phosphate, water-soluble chlorophyllins, antibiotics with free carboxylic groups, and many other compounds which have been suggested for toothpaste formulation, are similarly unusable because of their potential reaction and precipitation with strontium ion in the presence of water contained in the toothpaste.

Examples of water-soluble ionic strontium compounds that may be employed satisfactorily for the present purpose include strontium chloride, strontium acetate, strontium bromide, strontium lactate, strontium iodide, strontium nitrate, and strontium salicylate. However, the choice of the particular anion in the original dry strontium compound will be apparent from the above to those skilled in the art. The limiting circumstances are that the strontium compound used be non-toxic, that it be water-soluble, that it can be dissolved in the water contained in the toothpaste, and that it contribute strontium ions to the aqueous solution in which it is used. When the term "ionic" strontium compound is employed, what is meant is a strontium compound which provides strontium ions when in aqueous solution. When the term "water-containing" toothpaste is employed, what is meant is a dentifrice in semi-solid or viscous, liquid form which has been compounded with enough water to dissolve a substantial percentage or all of the strontium compound contained therein.

The concentration of the strontium ions employed in compatible toothpaste compositions should range from between about 0.5% to 10.0% and the surface-active wetting agent from about 0.5% to 5.00%. Concentrations of strontium ions lower than the stated minimum will have little effect in relieving hypersensitive dentin. Amounts in excess of 10% will result in salty and bitter toothpastes, rendering them unpalatable, although not detracting from their therapeutic utility. More particularly, it has been found that the range of 2.0% to 5.0% of strontium ions and 1.0% to 3.0% of the wetting agent to be preferable concentrations to exert the desired therapeutic effect. The compatible polishing agent should preferably be present by weight between about 10% and 50%. The amount of water used in the toothpaste composition should be great enough to dissolve a therapeutically active concentration of the water-soluble strontium compound within the limits set forth above.

As examples of toothpastes in accordance with the present invention, the following are offered for illustrative purposes, percentages being given by weight:

EXAMPLE 1

	Percent
Strontium chloride.6 H_2O	[1] 10.0
Water	36.2
Glycerin	25.0
Hydroxyethylcellulose	1.6
Polyoxyethylene sorbitan monolaurate	2.0
Micronized silica	24.0
Spearmint oil	1.0
Saccharin	0.2

[1] Equivalent to 3.3% strontium ion concentration.

EXAMPLE 2

	Percent
Strontium lactate.3 H_2O	[1] 8.0
Water	36.2
Strontium carbonate	15.0
Sodium N-lauryl N-methyltaurate	2.5
Sorbitol	20.0
Micronized silica	15.0
Methylcellulose	2.0
Peppermint oil	0.8
Dulcin	0.5

[1] Equivalent to 2.6% strontium ion concentration.

EXAMPLE 3

	Percent
Strontium acetate.½ H_2O	[1] 10.0
Water	27.00
Aluminum hydroxide	26.0
Micronized silica	10.0
Glycerin	22.0
Polyoxyethylene polymer (molecular weight about 2,000,000)	1.3
Polyoxyethylene lauryl ether	2.0
Spearmint oil	0.9
Methyl salicylate	0.1
Methyl para-hydroxybenzoate	0.05
Saccharin	0.15

[1] Equivalent to 4.2% strontium ion concentration.

EXAMPLE 4

("Liquid" Toothpaste)

	Percent
Strontium bromide.6 H_2O	[1] 20.0
Water	63.6
Micronized silica	10.0
Methylcellulose	2.0
Methyl parahydroxybenzoate	0.07
Propyl parahydroxybenzoate	0.03
Polyoxyethylene sorbitan monostearate	3.0
Spearmint oil	0.7
Peppermint oil	0.3
Saccharin	0.3

[1] Equivalent to 4.9% strontium ion concentration.

All of the above mentioned compositions are adequate cleansers for the human dentition and may be used for the ordinary purposes of removing superficial stains and food particles from and between the teeth, and for refreshing and sweetening the mouth. They differ from usual toothpaste formulations, however, in that in the presence of water contained in the toothpaste carrier, they release strontium ions which can connect and adsorb on the organic structure of dentin and thereby exert a protective effect against the transmission of sensory impulses from the exterior surfaces of the teeth to the dental pulp.

It should be noted that in the examples given above that the various ingredients thereof may be substituted in whole or in part by one or more of the similarly functioning substances earlier set forth and that the concentrations of these ingredients may be varied within the ranges earlier indicated.

While there has been described preferred embodiments of the present invention, it is apparent that numerous alterations, omissions and additions may be made without departing from the spirit thereof.

I claim:

1. A water-containing toothpaste comprising a substantially stable solution of a non-toxic, water-soluble ionic strontium compound and a surface-active wetting agent compatible with strontium ions in an aqueous solution, said toothpaste being characterized by the substantial absence of substances which precipitate said strontium.

2. The toothpaste of claim 1, wherein said surface acting wetting agent is selected from the class consisting of polyoxyethylene partial esters of polyhydric fatty acid derivatives, polyoxyethylene polyoxypropylene condensates, polyoxyethylene-fatty alcohol ethers and fatty acid N-methyl taurine condensates.

3. The toothpaste of claim 1, including a polishing agent selected from the class consisting of strontium phosphate, strontium carbonate, micronized silica and aluminum hydroxide.

4. The toothpaste of claim 1, wherein said strontium compound is selected from the class consisting of strontium chloride, strontium acetate, strontium bromide, strontium lactate, strontium iodide, strontium nitrate and strontium salicylate.

5. The dentifrice of claim 1, including a bodying agent selected from the class consisting of methylcellulose, hydroxyethylcellulose and polyoxyethylene polymers.

6. A water-containing toothpaste comprising a substantially stable solution of a non-toxic, water-soluble ionic strontium compound and a surface-active wetting agent compatible with strontium ions in an aqueous solution, said strontium ions constituting between 0.5% and 10% by weight of said toothpaste, said toothpaste being characterized by the substantial absence of substances which precipitate said strontium.

7. A toothpaste in accordance with claim 6, wherein said wetting agent constitutes between 0.5% and 5% by weight of said toothpaste.

8. A toothpaste in accordance with claim 7, including between 10% and 50% by weight of said toothpaste of a polishing agent compatible with strontium ions in an aqueous solution.

9. A water-containing toothpaste comprising a substantially stable solution of an ionic strontium compound selected from the class consisting of strontium chloride, strontium acetate, strontium bromide, strontium lactate, strontium iodide, strontium nitrate and strontium salicylate, a surface active wetting agent compatible with strontium ions in an aqueous solution and selected from the class consisting of polyoxyethylene partial esters of polyhydric fatty acid derivatives, polyoxyethylene polyoxypropylene condensates, polyoxyethylene-fatty alcohol ethers and fatty acid N-methyl taurine condensates, and a polishing agent compatible with strontium ions in an aqueous solution, said strontium ion constituting between 0.5% and 10% by weight of said toothpaste, said toothpaste being characterized by the substantial absence of substances which precipitate said strontium.

10. A toothpaste in accordance with claim 9, including a bodying agent compatible with said strontium ion.

11. A water-containing toothpaste comprising a solution of a non-toxic strontium compound providing strontium ions, a surface active wetting agent, a polishing agent, and characterized by the substantial absence of substances incompatible with the strontium ions in an aqueous solution.

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